

# ON PROBABILITY-DISTRIBUTION OF STATES IN RATIONAL THERMODYNAMICS\*

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**ABSTRACT.** In an essential statistical approach to thermodynamic problems, Dutta started with two observable entities, taken to be additive and having then numerical measures  $M$  and  $E$ . These quantities,  $M$  and  $E$ , corresponding to an instantaneous state (complexion), were assumed to be random variables. The probability-distribution for these  $M$  and  $E$  was taken to be exponential and written from arguments similar to those used for deduction of the Bayes rule. Then, the parameters of distribution were estimated by a method practically same as that of maximum likelihood. For an essentially statistical model, conceived in this way, all known results of statistical thermodynamics were obtained for equations of conservation of  $M$  and of  $E$ .

Here attempts are made to scrutinise earlier works to ascertain those properties of the above entities which play really fundamental roles in the development. It is seen that additivity (with usual physical assumption of continuity) implies and is implied by the exponential distribution, which is practically same as the Gibbs canonical (or, grand canonical) distribution in the terminology of orthodox statistical mechanics. Gibbs, starting from Liouville's theorem, proposed the canonical distribution as a distribution sufficient (not necessary) for constructing a mathematical model similar to thermodynamic systems. Here it is seen that it is necessary too. Then, how the statistical method of Dutta is related to the orthodox method of maximum likelihood of Fisher is investigated. Finally, the laws of probability-distributions for temperature, chemical potential etc., and expressions for their fluctuations are obtained.

## INTRODUCTION

In last fifteen years some attempts have been made to formulate and solve the problem of rational thermodynamics from essentially statistical and probabilistic methods with statistical model. The advantages of these attempts appears to be two-fold. Firstly, the methods are expected to be applicable also to systems which are not of thermodynamics nor even of physics. Secondly, it will be possible to interpret the equations and other results, commonly discussed in thermodynamics, in various ways in context of other branches of science thus, their real deeper significances will be revealed.

Starting with statistical model and using statistical arguments similar to Bayes rule, Dutta (1951, 1953, 1955, 1959, 1960, 1965a, 1965b), wrote down the

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probability distribution for states of a thermodynamic system and estimated the parameters, involved in the distribution by a method, closely related to that of maximum likelihood of Gauss and Fisher. Then, from the equation of conservation of any of the fundamental entities, written down suitably, all the known results of that of phenomenological thermodynamic in forms quite similar to those, obtained by Gibbs (1902) and Fowler (1936)

With some objectives, Jaynes (1957a, 1957b) obtained the probability distribution of states by the method, named by him as the maximum entropy estimation, by maximising the information theoretic entropy which came into great prominence after the development of information theory (Shannon and Weaver, 1949, Goldmann 1953; Khinchin, 1957). Then, he obtained the commonly known results of statistical thermodynamics by identifying some of the quantities, entered in his calculations with usual thermodynamic quantities after Schrodinger (1948).

Recently Mandelbrot (1963) also tried to study the statistical mechanics of Gibbs as a branch of statistics. In his opinion, in statistical mechanics the physicists, and in mathematical statistics the theoretical statisticians have been developing practically same methods from similar ideas in different symbols and different terminology without knowing and understanding works of one another.

Dutta (1960) showed that the laws of probability distribution of states, obtained by Dutta, and by Jaynes (1957a) were identical. As in both the developments, models, started with, are same and, also, the results obtained are same, so, it is quite natural to think that there must be deeper interrelations between these two for finding out the probability distribution of states. Recently, Mukerjee (1965) just touched this point from considerations of stochastic processes by simple mathematics. Dutta (1965a) also established that the method of maximum entropy estimation as used by Jaynes implies and is implied by an exponential distribution with parameters, estimated by the method, used by Dutta, and practically same as that of maximum likelihood of Gauss and Fisher. That the maximum entropy estimation leads to an exponential distribution is known (Kullback 1959), but that the parameters of the distribution by maximum likelihood has not been noticed earlier. Also, Dutta (1965) has been able to establish the deep interrelation even between the definition of likelihood function and that of information-theoretic entropy, particularly for ergodic samples, and between these two methods considered purely as methods of statistical estimation. In this connection, it is to be noted that if the frequency approach to probability as put forward by Venn, Mises, Crammer and others be accepted as most fundamental to start with the above results will be evident.

The aim of the present discussion is to investigate what basic properties of the entities, introduced by Dutta as most fundamental in his essentially statistical approach, leads to the exponential distribution and how. It is seen that it is not necessary that the exponential distribution should be introduced by advancing

the arguments, similar to the Bayes's rule. It is a simple and direct consequence of additivity (also known as, the extensive property)

Another object of this paper is to show clearly how the method of estimation, used by Dutta, is fitted in with the orthodox method of maximum likelihood of Fisher. In this connection the role of ergodic theory in these statistical developments has been pointed out clearly. The assertion of Jaynes (1957) that in essential statistical development the ergodic hypothesis is not at all necessary is not a fact. This point has just been mentioned by Dutta earlier (1965a). Here, this point has been dealt with in some details.

At the end, the probability distribution of the parameters of distribution (which are related to the temperature and the chemical potential) and then the expressions for functions of the temperature and the chemical potential have been deduced. These are quite in agreement with those given by Landau and Lifschitz (1958)

#### FUNDAMENTAL ENTITIES

Dutta in his essentially statistical approach (1951, 1953, 1956 and 1959), started with two entities, denoted by  $M$  and  $E$  which were supposed to be two observable entities specifying the system, under consideration in a state. The system considered was taken to be open, i.e., to be able to exchange these entities freely with the environment (in the orthodox language of thermodynamics, in a heat and matter both). As the fluctuations were also supposed to be fundamental for the system in a state, so the instantaneous numerical measures of  $M$  and  $E$  are random variables. The probability distribution of these quantities were written from arguments, similar to those used in discussions of Bayes rule and normalisation. The parameters of the distribution were estimated by method similar to that of maximum likelihood. How the method, actually used by Dutta, fits in with the orthodox method of maximum likelihood of Fisher is investigated in the section 5.

Besides the randomness, the additivity of  $M$  and  $E$  was postulated as the basic property. By additivity, it is meant that the instantaneous value of any of the quantities  $M$  and  $E$ , of a system consisting of a number of mutually non-interacting (statistically independent) part-systems is equal to the algebraic sum of its instantaneous values of the part-systems. The discussion of additivity can be seen in some standard literature of classical thermodynamics (Epstein, 1948). In a recent new axiomatic development of thermodynamics (Giles, 1964) the significance of the concept of additivity has been fully emphasized. The additivity is really the basic property of thermodynamic variable in standard literatures of thermodynamics (e.g., see Epstein, 1948, Guggenheim, 1950). In a recent paper (Dutta, 1965a), it has been explicitly asserted that 'for determining the correct law of distribution of states, the measurable quantities should be fundamental,

i.e., satisfying the additivity law and the conservation law'. The work 'correct,' in this assertion signifies just sufficient for probabilistic consideration and also 'just meeting thermodynamic requirements'. In the next section, it will be shown that randomness and additivity are just sufficient for complete determination (i.e., specification and estimation) of the probability distribution of states of the system.

For thermodynamic requirements i.e., for constructing functions having fundamental properties similar those of entropy, temperature and the like, and equation of conservation of any one these entities should be written. This equation is written by equating the total (small) increment of any of these entities due to small changes in the system and/or environment to the (algebraic) sum of the small changes in the coordinates, explicitly used for the system and environment along with changes due to flow or caused by changes of uncontrollable or hidden variables associated with the system or the environment. In the statistical approach, proposed by Dutta it is seen that the same expression of entropy is obtained as the integral of Paffian equation for conservation of any one of these entities after identification of these equations for interpretation with usual equations for conservation in physics, viz. the first law of thermodynamics, the equation of continuity, etc., but, the integrating factors are different and correspond to different physical quantities, viz. temperature, chemical potential, etc., which are the intensive variables of thermodynamic.

In the statistical approach by Dutta, entities, which are random, additive and conserving, are called 'fundamental'. Instantaneous values of mass, energy, charge momentum, etc. of a microscopic physical system are examples of the fundamental quantities. In the terminology of Giles (1964), additive conserving quantities are 'components of contents'. In the axiomatic discussion of Giles, it is seen that any components of contents may be taken as the basis for introduction of entropy. In Jaynes' approach (1963), it is also noted that the probability discussion can be made with any measurable quantity, but, the use of energy (not temperature) is most convenient for the purpose of thermodynamics. Some explanations for the necessity of taking energy as the basis in the statistical formulation of thermodynamics, put forward by Jaynes, are from mechanical consideration. This explanation, based on mechanical consideration defeats the very objectives of the essential statistical approach to thermodynamics for deducing everything from statistical model by statistical reasoning only.

#### ADDITIVITY RANDOM VARIABLE AND EXPONENTIAL DISTRIBUTION

Let  $M, E$  be numerical measures of two additive random entities of a system composed of two non-interacting (statistically independent) part systems, of which the corresponding quantities are  $M_1, E_1$  and  $M_2, E_2$  where

$$M = M_1 + M_2, \quad E = E_1 + E_2 \quad \dots \quad (3.01)$$

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As all these quantities are random variables so a probability distributions are associated with them. From additivity of  $M$  and  $E$ , and from the multiplicativity of the probability, we have

$$P(M_1 + M_2, E_1 + E_2) = P(M_1, E_1) P(M_2, E_2) \quad \dots \quad (3.02)$$

or

$$\log P(M_1 + M_2, E_1 + E_2) = \log P(M_1, E_1) + \log P(M_2, E_2) \quad \dots \quad (3.03)$$

where

$$\sum_{M, E} P(M, E) = 1 \quad \dots \quad (3.04)$$

the summation being taken over all values of  $M$  and  $E$

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**Prop** If  $g(x, y)$  be a continuous function of  $x$  and  $y$  satisfying the functional relations given by

$$g(x_1 + x_2, y_1 + y_2) = g(x_1, y_1) + g(x_2, y_2) \quad \dots \quad (3.05)$$

then,  $g(x, y)$  must be an exponential function.

**Proof** . Taking  $x_1 = 0, x_2 = 0, y_1 = 0, y_2 = 0$  we get

$$g(0, 0) = g(0, 0) + g(0, 0) \quad \dots \quad (3.06)$$

i.e.,

$$g(0, 0) = 0 \quad \dots \quad (3.07)$$

Obviously  $g(x, y) = 0$

is a trivial solution of (3.05)

Now, from the relation (3.05), it is easy to see that

$$g(na, 0) = ng(a, 0), \quad g(0, mb) = mg(0, b) \quad \dots \quad (3.08)$$

for any two numbers  $a$  and  $b$  and for any two positive integers  $n$  and  $m$ . Then, for integral  $n$  and  $m$ , we also have

$$\frac{1}{n} g(a, 0) = \frac{1}{n} g\left(n \cdot \frac{a}{n}, 0\right) = g\left(\frac{a}{n}, 0\right), \text{ and, } \frac{1}{m} g(0, b) = g\left(0, \frac{b}{m}\right) \dots \quad (3.9)$$

From these two relations, for integral  $p, q, p', q'$ , we have

$$g\left(\frac{p}{q} a, 0\right) = \frac{p}{q} g(a, 0), \quad g\left(0, \frac{p'}{q'} b\right) = \frac{p'}{q'} g(0, b) \quad \dots \quad (3.10)$$

Then, from continuity of  $g(x, y)$  we get

$$g(x'a, 0) = x'g(a, 0) \text{ and } g(0, y'b) = y'g(0, b) \quad \dots \quad (3.11)$$

for real  $x', y'$ . Thus, we can write

$$g(x, y) = g(x+0, 0+y) = g(x, 0) + g(0, y) = xg(1, 0) + yg(0, 1) \quad \dots \quad (3.12)$$

If  $x, y$  be negative, we have

$$0 = g(0, 0) = g(x+(-x), y+(-y)) = g(x, y) + g(-x, -y) \quad \dots \quad (3.13)$$

$$\text{or} \quad g(x, y) = g(-x, -y) = xg(1, 0) + yg(0, 1) \quad \dots \quad (3.14)$$

*Note* . In the above proof, it is to be noted that it is sufficient to take  $g(x, y)$  continuous with respect to  $x$  and  $y$  separately.

Now, as  $P(M, E)$  is a probability distribution, so,

$$P(M, E) = \frac{t^M z^E}{\sum t^M z^E} = \frac{t^M z^E}{f(t, z)} \quad (3.15)$$

$$\text{where} \quad f(t, z) = \sum_{n, E} t^M z^E \quad (3.16)$$

and in the summation  $\Sigma$ , the term is to be repeated if there be multiplicity of states specified by  $M$  and  $E$  (in the terminology of physics, degeneracy of states). It is to be noted in this connection that as  $P(M, E)$  is multiplicative, we should have

$$f(t, z) = f_1(t, z) \cdot f_2(t, z) \quad (3.17)$$

where  $f(t, z)$  is associated with the entire system and  $f_1(t, z)$  and  $f_2(t, z)$  are associated with part-systems. The validity of relations and its significance were considered in earlier papers (Dutta, 1953, 1956, 1965a).  $f(t, z)$  is the partition function.

The probability distribution given by (3.15), (3.16), and of course, originally written from different arguments was the starting point of the essential statistical approach of Dutta

In the above deduction, same set of  $t$  and  $z$  has been taken for both the part-systems. This means that they have been taken from the same (statistical) population, and in the language of statistical mechanics after Gibbs, the systems are known to be in statistical (thermodynamic) equilibrium.

#### THE FORMULATION OF GIBBS AND EXPONENTIAL DISTRIBUTION

Starting from Liouville's theorem,

$$\frac{dP}{dt} = [P, H] \quad \dots \quad (4.01)$$

Gibbs (1900) argued that for statistical equilibrium,

$$\frac{dP}{dt} = 0, \quad \text{i.e.,} \quad [H, P] = 0 \quad \dots \quad (4.02)$$

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For any constant  $C$  of motion of a dynamical system

$$[H, C] \quad \dots \quad (4.03)$$

and also, for any (differentiable) function  $F(c)$  of the constant  $C$  of motion

$$[H, F(c)] = 0 \quad \dots \quad (4.04)$$

Thus, from (4.02), it is sufficient to take that

$$P = f(C_1, C_2, \dots) \quad \dots \quad (4.05)$$

where  $C_1, C_2, \dots$  are constants of motion. (Gibbs, for simplicity, assumed the index of probability as a linear functions of constants. As in thermodynamics, energy is the most important concept and no other quantity associated with any other constant of a motion is generally introduced so in the major part of the development of statistical mechanics due to Gibbs, the canonical distribution (which is nothing but a general exponential distribution) is given by

$$P = e^{\frac{\psi - \epsilon}{\theta}} \quad \dots \quad (4.05)$$

where  $\psi$  and  $\theta$  are parameters of distribution and  $\epsilon$  is the energy of the system is taken as the starting point of discussion. In this development, one can also find a bit more general distribution, named by him as 'grand canonical distribution' and given by

$$P = e^{(\psi - \epsilon + \sum \mu_l N_l)/\theta} \quad \dots \quad (4.07)$$

where  $\psi, \theta, \mu_l$ s are parameters of distribution,  $\epsilon$  is the energy and  $N$ 's are the number of  $l$ -th type of particles. This is also an exponential distribution and can be written by same simple transformation of variables in the form (3.15). Besides these canonical distributions, in the entire development of Gibbs, the only other distribution considered is the uniform surface distribution on an energy-surface. But this is considered after Gibbs as a truncated canonical distribution and named as a micro-canonical distribution. In Gibbs' development, all these distributions are introduced as soon as possible distributions to suitable for construction mathematical models for thermodynamic systems, but, a little scrutiny will show that the canonical (exponential) distributions are only fundamental distribution for this purpose. Thus, canonical distributions are necessary and sufficient. Sufficiency was stressed by Gibbs himself. Necessity of the distribution is implied by additivity of energy and other significant constant of motion when required in particular cases.

### METHOD USED BY DUTTA AND THE ORTHODOX METHOD OF MAXIMUM LIKELIHOOD OF FISHER

Thermodynamic and similar other microscopic measurements are generally taken for a time  $T$ , sufficiently large, compared to the least time  $\tau$  required by a

[sense or a machine to get any impression (as for example, the time for eye is 1/10th. of a second). Thus the actually measured values are really over time intervals.

Let  $n_i$  be the frequency of realisation of a set of values of  $M$  and  $E$  in  $N = T/\tau$  intervals. If  $M_0, E_0$  be the observed values (i.e. the average values), thus,

$$M_0 = \frac{1}{N} \sum n_i M_i \quad \dots \quad (5.01)$$

$$E_0 = \frac{1}{N} \sum n_i E_i \quad \dots \quad (5.02)$$

In the essentially statistical approach proposed by Dutta, the expression,

$$P(M_0, E_0, t, z) = \frac{t^{M_0 z E_0}}{f(t, z)} = \left[ \Pi_l \left\{ \frac{t^{M_l z E_l}}{f(t, z)} \right\}^{n_l} \right]^{1/N} \quad \dots \quad (5.03)$$

has been maximised, where as in the orthodox method of Fisher, the likelihood functions,

$$L = \Pi_l \left\{ \frac{t^{M_l z E_l}}{f(t, z)} \right\} = P^N$$

is maximised. As  $N$  the sample size, remain constant in the variations considered and, evidently  $P = L^{1/N}$  and  $L$  attains maximum simultaneously, so the equations for determining are same.

In the statistical approach of Dutta, it is seen that these observed values are also the mean values of these two fundamental entities, calculated from distribution, and for other entities, mean values calculated from the distributions, have been taken to be equal to the observed values. In other statistical approaches, also, mean values calculated from the distributions are postulated to be equal to those observed values. Now, the postulate, by which mean values are equated to observed values (time-averages), is an ergodic hypothesis. Only, the form of this hypothesis may change when the mechanical model is replaced by a statistical model. Beside this hypothesis, as in usual statistical mechanics here also, we have to introduce another hypothesis for equating the short time-average (actually observed) values to the above long time averages. (Dutta, 1966). Thus, Jaynes impression that in these statistical approaches the discussions of ergodicity can be avoided appear not to be justified.

#### DISTRIBUTION OF $t, z$ AND FLUCTUATIONS OF TEMPERATURE ETC.

For the fixed observed values of  $M$  and  $E$ , the law of distribution for  $t, z$ , can be taken as usual as

$$p(t, z; M_0, E_0) = \frac{t^{M_0 z E_0}}{f(t, z)} = g(t, z; M_0, E_0) = e^{G(t, z)} \quad \dots \quad (6.01)$$



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Now by Taylor's expansion of  $G(t, z)$  about  $(t_0, z_0)$  the set of values of  $t$  and  $z$  estimated from likelihood equations we get

$$G(t, z) = G(t_0, z_0) + \frac{1}{2} \left\{ (t-t_0)^2 \left( -\frac{\partial^2 G}{\partial t^2} \right)_0 + 2(t-t_0)(z-z_0) \left( -\frac{\partial^2 G}{\partial t \partial z} \right)_0 + (z-z_0)^2 \left( -\frac{\partial^2 G}{\partial z^2} \right)_0 \right\} + \{\text{terms containing higher powers of } (t-t_0) \text{ and } (z-z_0)\} \dots \quad (6.02)$$

$$p(t, z | M_0, E_0) = C \frac{M_0 z_0 E_0}{f(t_0, z_0)} \exp \left[ -\frac{1}{2} \{ (t-t_0) \left( -\frac{\partial^2 \log g}{\partial t^2} \right)_0 + \dots \} \right] \dots \quad (6.03)$$

$C$  being the factor to be determined by normalisation ... (6.03)

Now from well-known results of statistics, fluctuations are given by

$$\text{Exp} \{ (t-t_0)^2 \} = \text{Var} (t) = - \frac{1}{\left( -\frac{\partial^2 \log g}{\partial t^2} \right)_0} \Delta \quad (6.04)$$

$$\text{Exp} \{ (z-z_0)^2 \} = \text{Var} (z) = - \frac{1}{\left( -\frac{\partial^2 \log g}{\partial z^2} \right)_0} \Delta \quad (6.05)$$

$$\text{Exp} \{ (t-t_0)(z-z_0) \} = \text{cov} (t, z) = - \left( -\frac{\partial^2 \log g}{\partial t \partial z} \right)_0 \left[ \left( -\frac{\partial^2 \log g}{\partial t^2} \right)_0 \left( -\frac{\partial^2 \log g}{\partial z^2} \right)_0 \right] \Delta$$

where

$$\Delta = 1 - \left\{ \left( -\frac{\partial^2 \log g}{\partial t \partial z} \right)_0 \right\}^2 / \left\{ \left( -\frac{\partial^2 \log g}{\partial t^2} \right)_0 \left( -\frac{\partial^2 \log g}{\partial z^2} \right)_0 \right\} \quad (6.07)$$

Now, the expressions for the partial derivatives of  $\log g$  can be calculated as in an earlier paper (Dutta, 1965b). They are the following

$$\left( -\frac{\partial^2 \log g}{\partial t^2} \right)_0 = \frac{(M - M_0)^2}{t_0^2} \quad \dots \quad (6.08)$$

$$\left( -\frac{\partial^2 \log g}{\partial z_0^2} \right)_0 = \frac{(E - E_0)^2}{z_0} \quad \dots \quad (6.09)$$

$$\left( -\frac{\partial^2 \log g}{\partial t \partial z} \right)_0 = \frac{(M - M_0)(E - E_0)}{t_0 z_0} \quad \dots \quad (6.10)$$

It can be easily seen (Dutta, 1953) that  $M_0, E_0$  are the average values of  $M$  and  $E$ .

Utilising the above results, we get

$$\text{Var}(t) = \frac{t}{(\bar{M} - \bar{M}_0)^2} \Delta \quad \dots \quad (6.11)$$

$$\text{Var}(z) = \frac{z_0^2}{(\bar{E} - \bar{E}_0)^2} \Delta \quad \dots \quad (6.12)$$

$$\text{Cov}(t, z) = \frac{t_0 z_0}{(\bar{E} - \bar{E}_0)(\bar{M} - \bar{M}_0)} \Delta \quad \dots \quad (6.13)$$

and

$$\Delta = 1 - \frac{\{(M - M_0)(E - E_0)\}^2}{(M - M_0)^2 (E - E_0)^2} = 1 - r_{M,E}^2 \quad \dots \quad (6.14)$$

$r_{M,E}$  denoting the correlation between  $M$  and  $E$ .

Now the correlation between  $t$  and  $z$  is given by

$$r_{t,z} = \frac{\text{Cov}(t, z)}{\{\text{Var}(t) \text{Var}(z)\}^{1/2}} = \frac{\left( -\frac{\partial^2 \log y}{\partial t \partial z} \right)_0}{\left\{ \left( -\frac{\partial^2 \log y}{\partial t^2} \right)_0 \left( -\frac{\partial^2 \log y}{\partial z^2} \right)_0 \right\}^{1/2}} \quad \dots \quad (6.15)$$

$$= \frac{(M - M_0)(E - E_0)}{(M - M_0)^2 (E - E_0)^2} = r_{M,E} \frac{z_0}{t_0} = r^{1/kT} \quad \dots \quad (6.16)$$

and

$$t_0 = e^{\mu} / RT \quad \dots \quad (6.17)$$

Then,

$$\frac{dT}{dz_0} = \frac{1}{k(\log z_0)^2} \cdot z_0 = \frac{kT^2}{z_0} \quad \dots \quad (6.18)$$

and similarly,

$$\left( \frac{\partial \mu}{\partial t_0} \right)_{z_0} = \frac{kT}{t_0} \quad \dots \quad (6.19)$$

Then,

$$\text{Var } T = \left( \frac{dT}{dz_0} \right)^2 \text{Var}(z)$$

$$\begin{aligned} & \frac{k^2 T^4}{z_0^2} \cdot \frac{z_0^2}{(E - E_0)^2 \cdot (1 - r_{E,M}^2)} \\ &= \frac{k^2 T^4}{k T^2 C_v} \cdot \frac{1}{(1 - r_{E,M}^2)} = \frac{k T^2}{C_v} \cdot (1 - r_{E,M}^2)^{-1} \quad (6.20) \end{aligned}$$

after substituting the value of  $(E - E_0)^2$  from previous calculations (Dutta, 1953, 1959, 1965a). This is the expression given by Landau and Lifschitz (1958) for the temperature fluctuations multiplied by the factor  $(1 - r_{E,M}^2)^{-1}$ . Similarly expression for fluctuation of  $\mu$  can be obtained.

The expression for fluctuation for  $T$  reduces to the value given by Landau and Lifschitz (1958) when

$$r_{M,E} = 0 \quad \dots (6.21)$$

i.e., random variables  $M$  and  $E$  are uncorrelated. Actually the value,  $\frac{k T^4}{C_v}$ , has been obtained when  $T$  and  $V$  are taken as independent variable so that  $r_{T,V} = 0$ . Thus the expression (6.20) yield a general form

The law of probability distribution of and so of temperature and chemical potential are given by (6.03) when the values of the coefficients of exponential quadratic form is given by (6.08), (6.09) and (6.10). The distribution is approximately Gaussian. Landau and Lifschitz (1958) have also used the Gaussian distribution for finding out expressions for fluctuations of thermodynamic quantities. Here, the distribution is obtained from the fact that and have been estimated from the principle of maximum likelihood.

# CONCLUDING REMARKS

Now, in quantum mechanical formulation particularly in axiomatic representation states of a system are represented by vectors in Hilbert space and physically observable quantities correspond to Hermitian linear (additive homogeneous) operators in this space (Dirac, 1947, Ludwig 1954). So the probability distributions, associated with these physically observable quantities appears to be deducible as exponential distribution of this linear operators by extension of above arguments. This deduction appears to be interesting and will be investigated fully in future.

The probability distribution of parameters estimated by methods similar to that of maximum likelihood as seen in the above discussion is Gaussian approximately. It is in conformity with Fisher's idea. He always took the Gaussian distribution for parameters estimated by the principle of maximum likelihood (1925).

From this paper and earlier papers it appears that the statistical mechanics can be studied as a pure problem of statistics. This study appears to be interesting and instructive

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#### REFERENCES

- Dirac, O. A. M., 1947. *The principal of Quantum Mechanics* 3rd. Edn., Oxford Univ. Press
- Dutta, M., 1951, *Proc. Inst. Stat. Conf* (vide. Bulletin of *International Statistical Institute*, **32** p 286
- 1953, *Proc. Nat. Inst. Sc. (India)*, **19**, 109.
- 1955, *Proc. Nat. Inst. Sc. (India)*, **21**, 373.
- 1959, *Proc. Sum. Inst. of Theor. Phys. at Mussonic (India)*, 291
- 1960, *Gnan O Vignan*, **13**, 737
- 1965a, *Zt. f. Phys. Chemec.*, **223**, 380
- 1965b, Communicated.
- 1966, *Statistical Physics* (Foundation). World Press, (in press)
- Epustou, P. S., 1947. *Textbook of Thermodynamics*, J. Wiley & Sons, N.Y.
- Fisher, R. A., 1922. *Phil. Trans. Roy. Soc. London*, **A222**, 30
- 1925, *Proc. Camb. Phil. Soc.*, **22**, 700.
- Fowler, R. A. 1936. *Statistical Mechanics* (2nd Edn.) Camb. Univ. Press.
- Gibbs, W., 1902, *Elementary Principle in Statistical Mechanics*, Yale Univ. Press, p. 109.
- Giles, R., 1964, *Mathematical Foundation of Thermodynamics*, Pergamon Press, Oxford
- Goldmann, S., 1953, *Information Theory*, Prentice Hall Inc., N.Y.
- Guggenheim, E. A., 1950, *Thermodynamics*, North Holland Pub., Amsterdam.
- Jaynes, E. T., 1957a, *Phys. Rev.*, **106**; 620; (b), *Phys. Rev.*, **107**, 171.
- Kninchin, A. T., 1957, *Mathematical Theory of Information*, Dover Publication, New York.
- Kullback, S., 1959, *Information Theory and Statistics*, John Wiley & Sons, New York
- Landau, L. D and Lifschitz, E. M., 1958, *Statistical Physics*, Pergamon Press, Oxford
- Ludwig, G., 1954, *Die Grundlagen der Quantum Mechanik*, Springer Verlag, Berlin
- Mandelbrot, Benoit, 1963, *Ann. Math. Stat.*, **33**, 1021.
- Mukherjee, T. K., 1965, *Science and Culture*, **31**, 528
- Schrodinger, E., 1948, *Statistical Thermodynamics*, Camb. Univ. Press, Cambridge. (1945)
- Shannon, C. and Weaver, Warren, 1949, *The Mathematical Theory of Communication* The University of Illinois Press, Urbana U.S.A.,